Journal of Babylon University/Pure and Applied Sciences/ No.(2)/ Vol.(23): 2015

Determination of Lead in Water, Roadside Soil, Plant and Blood in Basrah City – IRAQ

Muayad H.Mohammed Ali H. Amtehgy Amal A.Mahmood
Marine Science Centre Basrah Univ.
aamalachmed@yahoo.com aliamteghy2005@yahoo.com malbehadili@mscbasra.org

Abstract:

Lead pollution is one of the most important problems in Iraq and causes serious effects to humans and animals. The aim of the present study was to evaluate the spatial distribution of lead in main areas of Basrah.Analytical study of lead pollution in Basrah city is carried out. The study included water, dust of sides of the roads, leaves of plants and blood samples from different peoples. Basrah city was divided into different stations from Qurna to Fao.Eight stations for water and 12 stations for dust collected from roadside, plant leaves from 12 stations were also collected. The study also considered 40 blood samples due to the importance of blood pollution of lead. Standard method for determination of lead is taken into account. Water samples were preconcentranted by evaporation and atomic absorption spectrophotometry is then used for quantitative measurement of the final extract. Dust of road sides were extracted with EDTA and then measured after dilution by atomic absorption spectrophotometry. Dithizone spectrophotometry is considered common and simple technique; therefore it is used for extraction of lead in leaves and blood. Levels of lead are follows: for water: (0.009 – 0.071) mg / L lead was found, the highest levels of lead is in Ashar river. The lowest level is found in Euphrate river – Qurna, for roadside soil (dust of the road sides): the range of lead was (112 –350) µg / g. The highest pollution is in Marbad square (City Centre) while the lowest value is in Hamdan (Abu Al-Khaseib), for leaves: the range of lead was (0.47 – 3.01) µg / g. Highest levels in Marbad square and the lowest is in university garden in Karma, and for blood: the highest value of lead 66 µg/100 ml is found in traffic officer with 34 years service. The lowest value was found 8 µg/100 ml in child of village respectively

Key word:trace metals , water , lead , plant , blood , pollution , basrah

الخلاصة

التلوث بالرصاص هي واحدة من اهم المشاكل في العراق والتي تسبب تأثيرات خطيرة على البشر والحيوانات هدفت الدراسة الحالية لتقييم التوزيع المكاني للرصاص في المساحات الرئيسة في مدينة البصرة. أجريت دراسة تحليلية لتقدير نسب الرصاص في مدينة البصرة باستخدام نماذج بيئية من مناطق مختلفة امتدت من القرنة وحتى الفاو تمثلت بثمانية نماذج من مياه الأنهار و12 نموذج من الأتربة المتجمعة عند جوانب الطرق و12 نموذج من الأوراق النباتية.كما تضمنت الدراسة 40 نموذجا للدم من أشخاص مختلفي المهن والأعمار من سكان المحافظة من ضمنهم 11 نموذجا لرجال شرطة المرور.استخدمت الطرق القياسية العالمية في التقدير.ففي نماذج المياه تم تركيز الرصاص بالتبخير ثم قياسه باستخدام مطياف الامتصاص الذري اللهبي ولنماذج التربة الجانبية للشوارع تم استخلاص الرصاص بالاثيلين ثنائي أمين رباعي حامض الخليك (EDTA) ثم تقديره بمطياف الامتصاص الذري.طبقت الطريقة اللونية على نماذج الدم والأوراق النباتية بعد استخلاص الرصاص باستخدام كاشف الدايثيزون.وكانت النتائج كالتالي: لمياه الأنهار وجد أن تركيز الرصاص بين (0.009 – 0.071) ملغم \ لتر حيث كانت أعلى قيمة في نهر العشار بينما أوطأ قيمة في نهر الفرات – القرنة،وفي التربة (المتساقطات من جوانب للشوارع) كان معدل تركيز الرصاص بين (112– 350) مايكرو غرام \ غرام، حيث كانت أعلى قيمة في ساحة المربد (مركز مدينة البصرة) وأوطأ قيمة عند جانبي شارع حمدان – قضاء أبو الخصيب،وفي الأوراق النباتية تراوحت تراكيز الرصاص بين (0.47 – 3.01) مايكرو غرام \ غرام حيث كانت أعلى قيمة في ساحة المربد بينما أوطأ قيمة في المبنى الداخلي لجامعة البصرة في الكرمة، ولنماذج الدم وجد أن أعلى معدل لتركيز الرصاص قد بلغ 66 مايكرو غرام \ 100 مل عند احد رجال المرور الذي يعمل في المهنة منذ 34 سنة بينما كانت أوطأ قيمة 8 مايكرو غرام \ 100 مل عند احد الأطفال من سكنة الأرياف على التوالي.

الكلمات المفتاحية : عناصر نزرة ، ماء ، رصاص ، نبات ، دم ، مدينة البصرة

Introduction

Lead (Pb) is a natural constituent of the Earth’s crust, and is commonly found in soils, plants, and water at trace levels. Lead is a persistent toxic element that can accumulate in humans, animals and plants. Occurrence of metallic lead in nature is rare. The word lead derives from the Anglo-Saxon *leaden*, and the symbol Pb, from the Latin word for lead, *Plumbum*. Lead is by far the most abundant (13ppm) heavy element in the earth's crust. It is one of the few metals that can be found in metallic form in nature (rather than in compounds that must be reduced to extract metal). Lead a lustrous bluish-white metal, is very soft, highly malleable, ductile and a relatively poor conductor of electricity. It is highly corrosion resistant but tarnishes under exposure to air (Greenwood and Earnshaw, 1989). The main ore minerals of lead are galena (PbS) and cerussite ($PbCO_3$); anglesite ($PbSO_4$) and pyromorphite ($Pb_5(PO_4)_3Cl$) are less important, but occur frequently (Crook, 1921). Lead is usually found in ores that also contain copper, zinc, and silver, and is extracted as a co-product of these metals. Occurrence of lead ores is widespread, and lead is highly malleable and ductile, and easy to smelt. It is one of the seven metals of antiquity and the use of lead probably predates those of copper and bronze. The earliest known Pb artifact dates to 6500 B.C., while is believed that the processing of Pb minerals improved greatly about 6000 years ago (Nriagu, 1983). Lead has become the most widely scattered toxic metal in the world as a result of man's actions. Today, Pb is used widely in building construction, lead-acid batteries, bullets and shot, weights, solder, pewter, and fusible alloys. The presence of lead in excessive quantities will cause the hazard to the environment. Therefore its online monitoring has been paid more attention by responsible authorities.

Pollution caused by anthropogenic Pb originates mostly from mining, smelting, industrial uses, waste incineration, coal burning, and leaded gasoline. Lead is a toxic heavy metal that can enter human body through inhalation and ingestion from a variety of sources such as contaminated air and water, soil, and food. Lead poisoning in adults can affect the peripheral and central nervous systems, kidneys, and blood pressure (Needleman, 2004). Children are more susceptible to Pb than adults, with exposure to Pb causing irreversibly effects on the cognitive performance during childhood (Hilary, 2001). Lead pollution has become a cause of major concern since the early 1970s, which led to the banning of lead additives (the major source for anthropogenic releases of Pb) in gasoline in the western world since the mid-1970s. In recent years, the focus on lead poisoning has shifted away from adults exposed to high doses in industrial settings to the larger population of asymptomatic children with lesser exposures (Needleman, 2004).

In environmental investigation it is important to be able to determine the source of pollution and to characterize the transport history of the pollutants. Pinpointing the sources of lead pollution can be difficult because of the large number of potential Pb sources in typical urban settings, such as emissions from industrial sources, exhaust from gasoline vehicles, leaded paint, leaded pesticides, and even natural geological materials (bedrocks and soils). The sources of Pb and the contribution from each source cannot be inferred from the total Pb concentrations measured in environmental media (e.g., air, water, and soil) or human bodies (e.g., blood). This often puts the Clean up liability under dispute, slowing down the remediation process (Morrison, 2000). Furthermore, the ''true'' Pb source may continue to pollute the environment if the pollution is attributed to an incorrect source. Traditional approaches rely heavily on statistical analysis of large databases of samples to identify the sources and pathways of heavy metal contamination (e.g., Facchinelli *et al.*, 2001; Qishlaqi and Moore, 2007). Chemical composition has been used extensively to determine the source of materials by fingerprinting the chemical composition of the material to be identified and comparing it to those of the potential sources. The ratios of Pb and other heavy metals may help to establish the sources of pollution (e.g., Franco-Uria *et al.*, 2009; Zhang *et al.*, 2008). However, such analysis requires large databases and sophisticated statistics to provide results that may be equivocal due to poor correlation between variables and the possible presence of confounding factors.

Identification of the source of contamination, the timing of the release, and pollutant transport pathway and distribution in the environment are common issues in investigation and mitigation of lead pollution.

Many analytical techniques have been developed for determination of lead, such as colorimetric analysis (Abbaspour *et al*., 2006), UV-VIS spectroscopy (Cornrd *et al*., 2006), and either flam or graphite furnace atomic absorption spectrometry (AAS)(Panichev *et al*., 2005). In addition to these techniques, methods for multielemental determination have been developed, such as ion chromatography(IC)(Zeng *et al*., 2006; Shaw and Haddad, 2004) and inductively coupled plasma combined with either atomic emission spectrometry (ICP-AES)(Turkmen and Ciminli,2007) or mass spectrometry (ICP-MS)(Sahan *et al*., 2007; Goulle *et al*., 2005). In this study, we aimed to investigate lead accumulation in water, soil, plant and blood in the investigation area of Basrah city southern of IRAQ to evaluate the effect of Pb toxicity in humans and to determine the effect of lead toxicity on some growth parameters.

Study area and sampling sites

The city of Basrah is located on the west bank of the Shatt al-Arab River at a distance of 140 km from its mouth in the Arabian Gulf. There are five main branches connected to the river in the city of Basra, they are: AL-Rebat, AL-khandak , AL- Ashar , Al Khora and Al-Sarraji for a distance of 3, 2.5, 3, 4, and 4 km respectively. Al-Sarraji branch is mainly an agricultural irrigation channel while the remaining four branches are regarded as channels of discharging sewages and landfill waste for the city. Figure 1 shows the map of the city of Basra, the main rivers and locations of samples.

Materials and Methods

Eight water samples from river (W) were collected from the crowded city of Basra, their regions and other densely populated as well as the dimensions of the Shatt al-Arab River. The samples were preserved in plastic bottles (5L) and 1cm^3 of concentrated HNO_3 was added to each sample to avoid microbial activity.

Twelve soil samples (S) were collected from different places of the province, including dust of the traffic road side, at a distance of one meter from the road way, and heavy traffic square and streets as well as banks of the rivers

Twelve leaves plant samples (L) were also obtained from trees close to the squares, streets, and car parks. Moreover, certain samples were obtained from other places of less traffic. Collected samples were placed in a sealed plastic glass (Christian, 1986).

Forty blood samples were obtained from people different ages, professions, and sex of the population of the province, including 11 samples for the traffic police. 5 ml sample size was put in glass tube and preserved at 4 º C (Sthapit and Ottaway, 1984). History collection forms during the period between 25 - 12 - 2010 and 15 - 01 to 2011.

Preparation and analysis of water samples

Lead stock solution (1000 mg/ℓ): The stock Lead (II) solution was prepared by dissolving 1.5985g of lead nitrate ($Pb(NO_3)_2$) in deionised water containing 10 ml conc.HNO_3 and diluting the volume in a 1000-ml volumetric flask. This solution is then transferred to a polyethylene bottle. From this stock solution 1, 2، 3، 4 and 5 ppm solutions were prepared by dilution.

Digestion of water samples were carried out by taking 50 ml of water sample in a glass jar and then add to 5 ml of conc. nitric acid to each sample independently , and then placed over the heated laminated until evaporation to dryness, then repeated again ,using 5 ml of conc. nitric acid and evaporation continued again until dryness

and then completed to the original volume of 50 ml with distilled water. Keep in refrigerator prior to analysis; determine concentrations of lead by Atomic Absorption spectrophotometer (AA320N) (Chapman and Pratt, 1961).

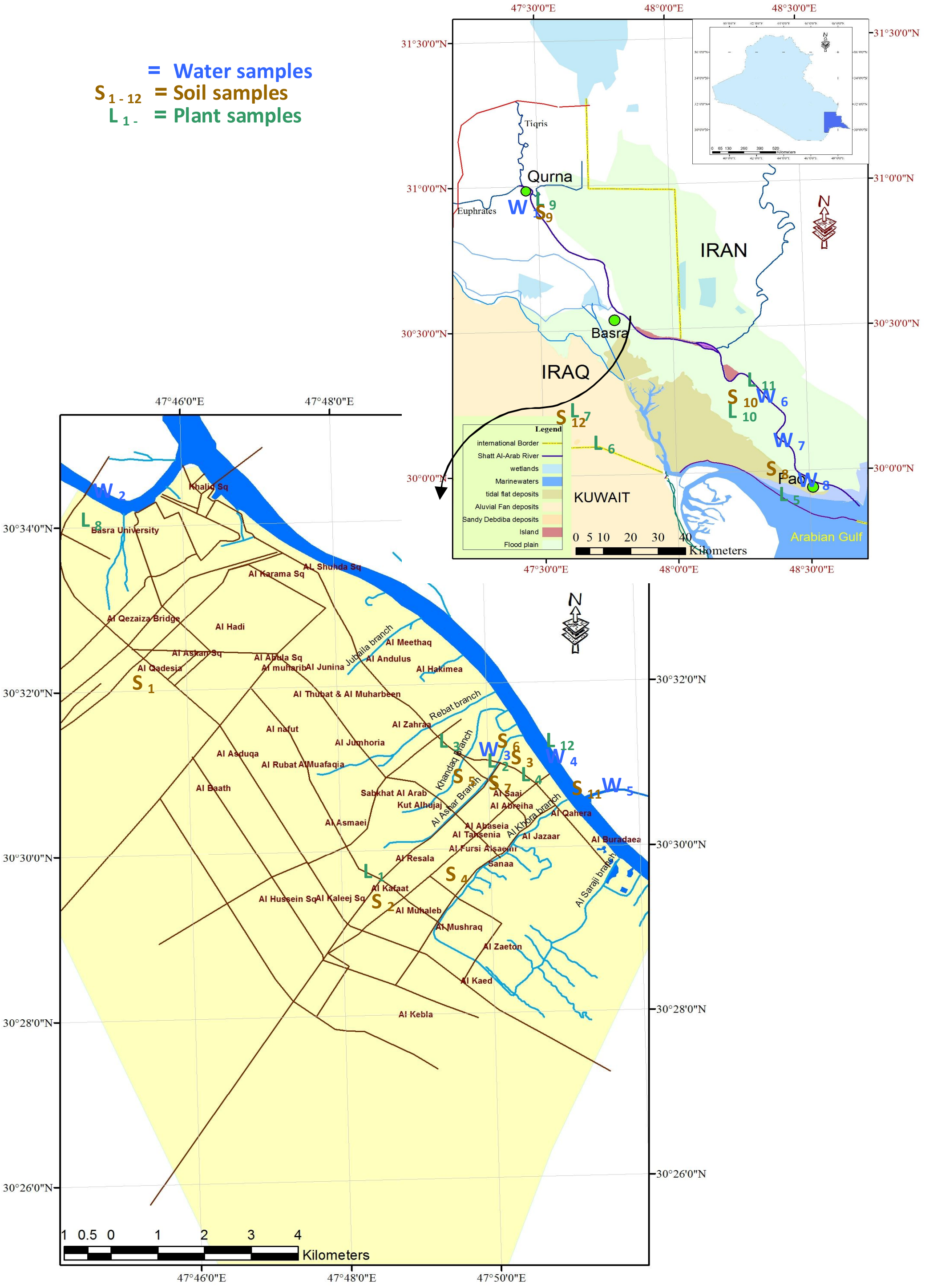

Fig.1. Map showing the studied area with sampling stations

Preparation and analysis for samples of roadside soil

Disodium ethylene Di amine Tetra Acetic acid (Na_2EDTA, 0.05M) :The aqueous solution of 0.05 M EDTA was prepared by dissolving18.6 g in a liter of deionized water

.Then a series of standard solutions of lead nitrate 2, 5, 10, 15, 25 mg / l were prepared. The samples of roadside soils were placed in clean plastic bags. All the samples were immediately transferred to the laboratory, air dried and placed in oven at 80 °C over night .The dry samples were homogenized by grinding using mortar and pestle. Samples of roadside soil were sieved through 2 mm mesh. Then about 15 g of the soil sample weighed and put in a100 ml conical flask .samples then are shacked for one hour in a shaker using 75 ml of 0.05 EDTA solution (neutralized to pH 7.0 with NH_40H ,pH-measurements were carried out using WTW, listed 8f93(Germany).The solutions were filtered off and the filtrates were analyzed for lead by AAS. Absorbance of standard solutions prepared were also measured (Lindsay and Norvell, 1978; Mench *et al*., 1994).

Preparation and analysis of plant leaves sample

Dithizone (1x 10^{-3} M): the solution of dithizone (1x 10^{-3} M) was prepared by dissolving 7.5 mg dithizone in 300 ml of methylene chloride. The mixture (ammonia - cyanide - sulfite) was prepared by dissolving 350 ml of concentrated ammonia solution with 30 ml of 10% potassium cyanide and 1.5 g sodium sulfite, then completed the volume to 1 liter with deionized water. The plant leaves samples were collected at each indicated distance, if present, and transported to the laboratory in polyethylene bags. plants leaves were washed with demineralized water and dried at 60°C for 24 hours, ashed at 450°C for 24 hours, then 5 grams from each ashed sample were digested in 10 ml concentrated nitric acid, filtered and diluted to 100 ml with distilled water(ROPME, 1982).

A 20 ml of the sample heated and adjusted for pH=2 then the solution is transferred to in 100 ml of Baker. Add two drops of thymole blue and evidence is of ammonia solution (2 M) until the color changes to blue. The solution is transferred to a separating funnel and 250 ml added to 60 ml of reagent (ammonia - cyanide - sulfite). Followed by adding 25 ml of a solution of dithizone - methylene chloride with shaking for a minute. Separate layers then the organic layer of methylene chloride was filters and absorbances Measured by Philips Company model PU 8670 Vis/NIR spectrophotometer at wave length of 510 nm. Continue the work on the volume of 20 ml of 5, 4, 3,2,1,0 mg \ liter of each standard solutions of lead for the purpose of a calibration curve (Sandell and Onishi, 1978).

Preparation and analysis of blood sample

Dithizone solution (0.1%): was prepared by dissolving 0.025 g of dithizone in chloroform and made up to 100 ml, the solution of (acetate - cyanide) was prepared by mixing 30 ml of 10% potassium cyanide with 3 ml of 50% ammonium acetate and 10% of ammonium hydroxide and then complete to a volume of liter-deionised water . 5 ml of blood is transferred to a Kjeldahl flask, with two glass beads, 50 ml of nitric acid, and 4 ml of sulfuric acid. Heat gently at first to minimize foaming, and then slowly increase heat until boiling. Continue to heat slowly until volume is reduced to approximately 1/4 original volume (about 10 ml). Remove flame and then add 9 ml of a mixture (6 ml nitric acid plus 3 ml 72% of perchloric acid). Replace the flame and heat slowly until all the nitric and perchloric acid is driven off. This usually occurs when the volume is below 5 ml and the solution become pale yellow and clear, and copious SO_3 fumes are evolving. Continue by gently heat for 2-3 minutes to remove all perchloric acid.. The specimen is now completely digested and the residual volume is about 2 ml. Cool and then Add 3 ml of 50% ammonium acetate 50 ml of ammonium hydroxide, followed by adding 10 ml of reagent (acetate - cyanide), transfer the mixture into a separating funnel , then shaking for half a minute with 0.1% dithizone – chloroform layer and 10 ml of chloroform. Separate organic and water layers. Organic layer washed four times with washing solution. filter the solution and all the standards and samples were diluted to final volume of 25 ml using chloroform before absorbance measurement spectrophotometry at 525 nm .using (chloroform) reagent blank as a reference . Follow the same steps above for the preparation of standard solutions of lead for calibration curve using the Micro 10, 20,30,40,50,60,70,80 g / 100 ml.

Results and Discussion

According to previous procedure mentioned, the results obtained from calibration curve using absorbance for river water (the values of abs. magnified 20 times), roadside soil, plant leaves and blood Samples are given in tables (1, 2, 3 and 6) and fig. (2, 3, 4, 5) respectively. The trend of calibration is linear in range 0.05 - 5 mg / L.

Table 1: Concentration of Pb (mg / L) in water samples

Sample No.	1	2	3	4	5	6	7	8
Concentration	0.18	0.62	1.42	0.22	0.40	0.58	0.22	0.34
R.S.D	1.2	1.1	1.7	2.5	2.3	1.1	0.9	1.6

Table 2: Concentration of Pb (µg / g) in roadside soil samples

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12
Concentration	255	220	193	290	350	273	244	195	168	112	141	156
R.S.D	1.9	1.7	2.7	1.9	2.2	2.6	1.8	2.6	2.0	2.5	1.1	1.4

Table 3: Concentration of Pb (µg / g) in plant leaves samples

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12
Concentration	1.83	2.81	3.01	2.76	0.95	1.74	2.02	0.47	1.70	0.64	0.51	0.90
R.S.D	1.2	1.7	1.1	2.6	0.9	1.3	2.9	1.1	2.7	0.8	1.3	1.0

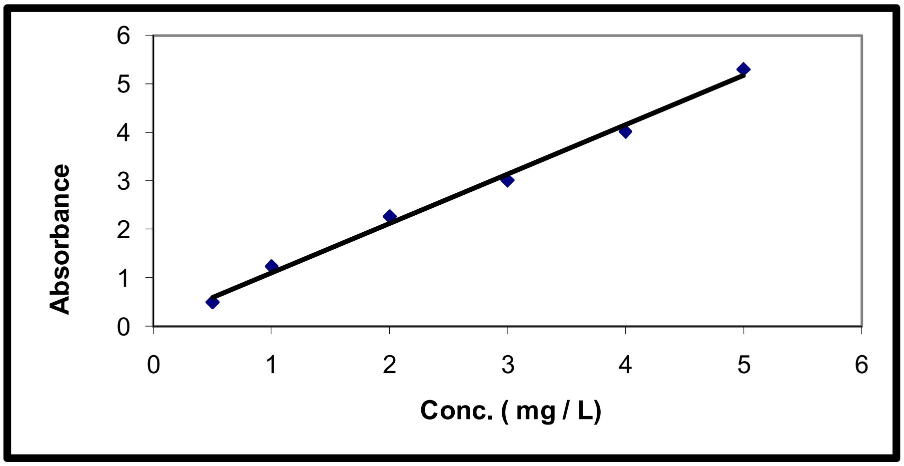

Fig 2: Calibration curve of Pb in water samples

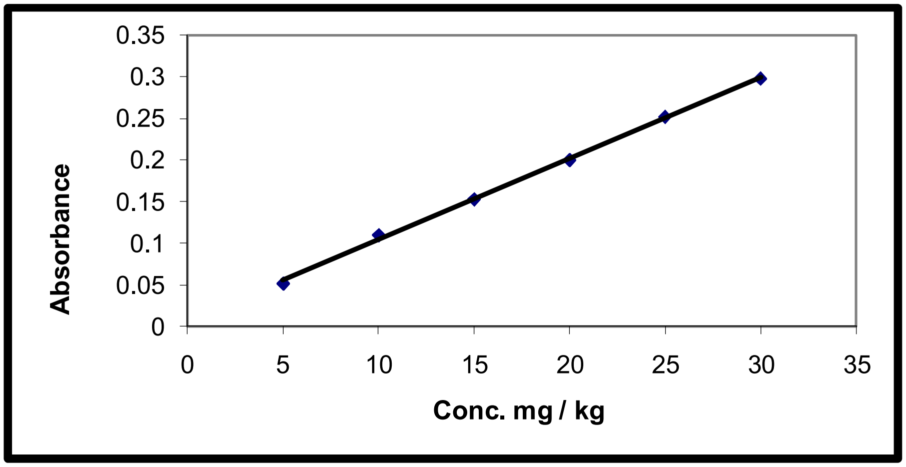

Fig 3: Calibration curve of Pb in roadside soil samples

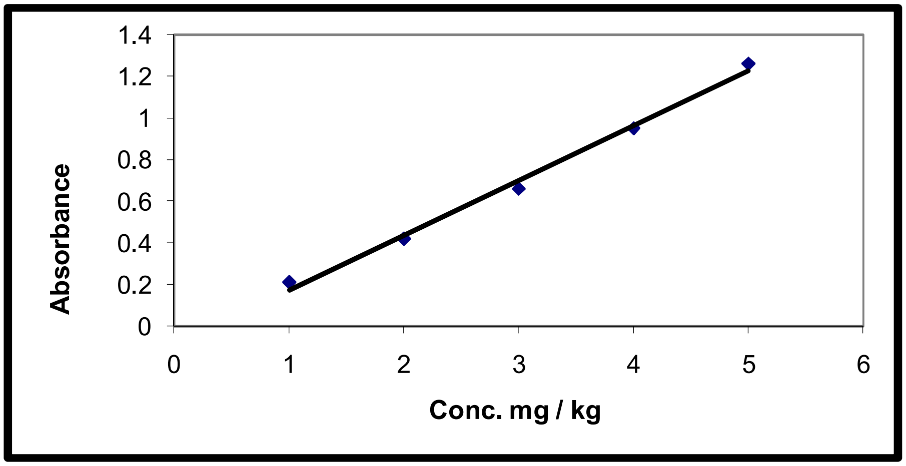

Fig 4: Calibration curve of Pb in plant leaves samples

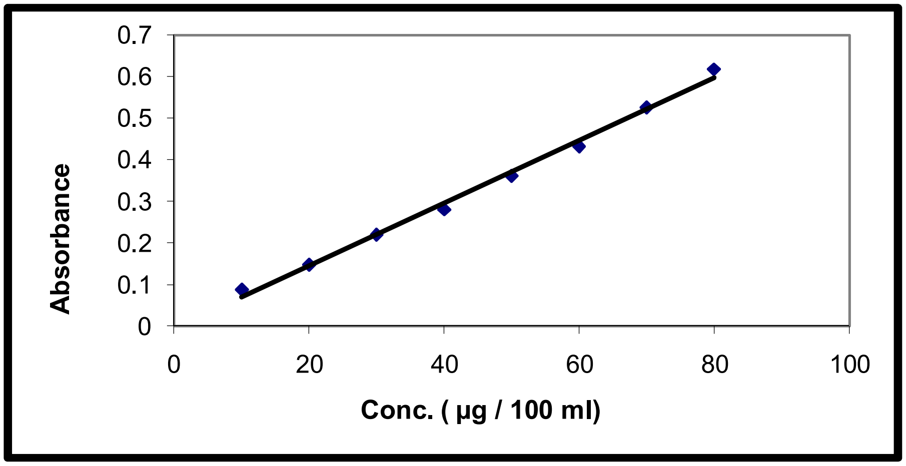

Fig 5: Calibration curve of Pb in blood samples

The accepted level of lead in water is 0.005 mg / L according to WHO / FAO (WHO / FAO, 2007), our results show (tab.1) which was in the range of (0.009 – 0.071), Ashar station (3) is the highest level because of domestic and highly populated station and due to the high number of vehicles that existed there which in contributed from lead emitted from these automobiles. While river and rain water which contribute substantially in rising lead level. In fact, in Basrah city centre, no factories or industrial emission are found therefore, the increase in lead is mainly due to emission from the crowd automobiles in the city centre and high discharge of sewage in branches which leads to Shatt-al-Arab River.

In Qurna city (70 km away from Basrah) which is opened stations and low number of vehicles that emitted lead to the air and low discharge from sewage, with no high lead concentrations. Therefore, it is the lowest point for lead.

Lead is accumulative heavy metal which concentrated in dust and roadside soil, then transferred to ground water and finally reached plants and human.

From table (2) the lead level in streets and square are (112 – 350) µg / g, which indicate that the highest level (350 µg / g) at Al-Merbed square in city centre, due to the highest crowded automobiles and surrounded with human activities. While Hamdan (10 km away from Basrah gave (112 µg / g) because of low number of automobiles and it was not crowded with building and human activities. The high mean value of the concentrations attested to the overall high level of contaminations of this metal in the roadside environment. This is in agreement with the report of Lagerwerff and Specht (1970). The high concentration of lead observed could be attributed to lead particle from gasoline combustion which consequently settles on roadside soils. Vehicles are often moving slowly as a result of the heavy traffic jam in this area and this may account for the high level of lead. This is in line with Francek (1992) report that traffic junction and cross roads, records higher levels of metals. Though, the high mean soil level confirms that the roadside environment is generally lead enriched despite a relative low traffic volume compared to other studies (Ho *et al*., 1987). The mean lead level observed is far lower than that reported by Ho *et al*. (1987) and Francek (1992).

Lead, the element of most concern in environmental heavy metal pollution, exhibited high levels of contamination as we got closer to the highway. Decrease elemental concentration with distance from the highway would indicate surface soil contamination by extraneous sources. Whereas unchanging levels would show that the heavy metal concentrations were a function of the soil itself. Since the fuel used by automobiles in Basrah is mostly leaded, the most probable source of such contamination is the lead particulate matter emitted from gasoline vehicles which settles not far from highway (Harrison and Laxen, 1981). As the distance from road increased, the Pb level fell sharply reaching the normal soil lead level, which was estimated to be less than 7 µg / g. Therefore, the lead contamination of soil was restricted to short distance from both sides of the highway. However, some investigations found that lead contamination of soil may reach 100 m from the main road (Jaradat and Mamoni, 1999). The average of lead 1.5 m east the road was much lower than those found in Hong Kong, North Wales Auckland and London, and it is comparable with that found in Birmingham, Ecuador, Nigeria and Amman as shown in tab. 4.

Table 4: The levels of Pb (µg / g) in roadside compared with other studies worldwide

Place	Conc. Pb	Ref
Basrah	112 – 350	This study
Amman	188.8	Jaradat and Mamoni, 1999
Hong Kong	991	
Ecuador	293	
Nigeria	247	
North Wales	1779	
Auckland	1650	
London	513	
Birmingham	205	

The roadside soil is the dominate source for lead contamination, the precipitation and air pollution. Both contribute substantially to lead increase in plants. Therefore, Merbed (3) reached 3.01 µg / g on plant surfaces, while the lead levels were low 0.47 µg / g at karma University gardens. Therefore, plants analyses are considered another indicator for lead pollution from water and roadside soil. Table 5 summarizes a comparison between our results and some other worldwide. The lead level in this study was much lower than that of others. This could be due to different plant types and different number of vehicles per day in those places.

Table 5: The levels of Pb (µg / g) in plants compared with other studies worldwide

Place	Conc. Pb	Ref
Basrah	0.47 – 3.01	This study
Amman	7.3	Jaradat and Mamoni, 1999
Hong Kong	134	
Auckland	180	

Determination of lead in blood:

The final conclusion from previous studies toward the analyses of lead in blood are present in table (6) which appeared that the concentration is (8 – 66) mg / 100 ml and the highest level is found in traffic person and increasingly with years of work at streets. Also, average concentration in men was more than in women. 14 toxicity cases were found (conc. of Pb > 40 – 100 mg / 100 ml), within those 8 cases of traffic personal (11 samples).

The highest concentration was in one traffic man which works for 34 years, while the lowest level was in child of village of Marshes. Figure (6) show gender, age and profession in lead level.

Table 6: Concentration of Pb in blood samples

Sample No.	Gender	Age (Years)	Occupation -Site	Length of service (Years)	Pb Conc. µg / 100 ml
1	Male	30	Traffic person	3	40
2	Male	20	Traffic person	2	21
3	Male	24	Traffic cop - Directorate of Traffic	4	30
4	Male	45	Traffic person	16	47
5	Female	27	Employee - Directorate of Traffic	4	41
6	Male	39	Traffic person	12	50
7	Male	33	Traffic person	7	43
8	Male	21	Traffic person	1	26
9	Male	53	Traffic person	34	66
10	Male	41	Traffic person	20	41
11	Male	50	Traffic cop - Directorate of Traffic	30	58
12	Male	24	Municipality factor	6	30
13	Female	23	Teacher - City Center	3	19
14	Female	13	Schoolgirl - Countryside	-	12
15	Male	40	Taxi driver	15	44
16	Male	30	Employee – State company of fertilizers	7	37
17	Male	27	Factor - Gas station	4	38
18	Female	30	Housewife	-	30
19	Female	14	Schoolgirl - Countryside	-	13
20	Male	38	Professor	10	37
21	Male	24	Engineer	1	30
22	Female	30	Doctor	5	28
23	Male	8	Studentt - Countryside	-	8
24	Male	41	Blacksmith – Industrial Zone	22	55
25	Male	30	Employee	11	39
26	Male	17	Student - City Center	-	24
27	Female	40	Housewife	-	30
28	Male	15	Studentt - Countryside	-	13
29	Male	20	Municipality factor	2	35
30	Male	33	Electricity factor	7	42
31	Male	40	Employee	17	35
32	Male	50	Farmer	20	30
33	Male	19	driver	3	39
34	Male	45	driver	25	51
35	Male	16	Studentt - Countryside	-	15
36	Male	30	Walker	10	43
37	Male	37	Teacher - Countryside	15	30
38	Male	27	Employee	6	40
39	Male	31	Doctor	6	38
40	Female	18	Student - City Center	-	33

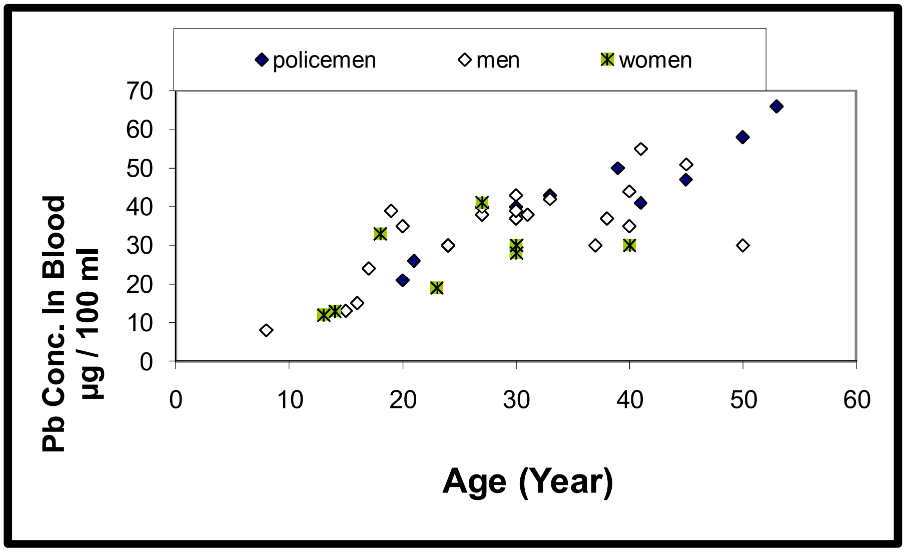

Fig 6: Effect of gender, age and profession in lead level.

References:

Abbaspour, A., Mehrgardi, A., Noori, A., 2006. Speciation of iron(II), iron(III) and full-range pH monitoring using paptode: a simple colorimetric method as an appropriate alternative for optodes [J]. Sensors and Actuators B 113(2):857-865.

Chapman, H.D. and Pratt D.F. (1961). Methods of analysis of soils, plants and water. University of California, Davies, Division of Agr. Sci., p. 309.

Cornard, J.P., Caudron, A. and Merlin, J.C., 2006. UV-visible and synchronous fluorescence spectroscopic investigations of the complexation of Al(III) with caffeic acid, in aqueous medium[J]. Polyhedron 25(11): 2215-2222.

Crook, T., 1921.Economic Mineralogy. A Practical Guide to the Study of Useful Minerals. Longmans, Green and Co., London.

Facchinelli, A., Sacchi, E., Mallen, L., 2001. Multivariate statistical and GIS-based approach to identify metals sources in soils. Environmental Pollution 114, 313-324.

Francek M.A 1992. Soil lead levels in a small environment: a case study from Mt. pleasant, Michigan. Environ. Pollut. J., 76: 251 – 257.

Franco-Uria, A., Lopez-Mateo, C., Roca, E., Fernandez-Marcos, M.L., 2009. Source identification of heavy metals in pastureland by multivariate analysis in NW Spain. Journal of Hazardous Materials 165, 1008-1015.

Greenwood, N.N., Earnshaw, A., 1989. Chemistry of the Elements. Pergamon Press, Oxford.

Goulle, J.P., Mahieu, L., and Castermant, J., 2005. Metal and metalloid multi-elementary ICP-MS validation in whole blood, plasma, urine and hair. reference values [J]. *Forensic Science International* 153(1): 39-44.

Harrison R.M and Laxen D.H., 1981. Lead pollution, Causes and Control. New York, Chapman and Hall.

Hilary, A.G., 2001. The biological chemistry of lead. Current Opinion in chemical Biology 5, 223-227.

Ho Y.B, Tai K.M (1988). Elevated levels of lead and other metals in roadside soils and grass and their use to monitor aerial metal depositions in Hong Kong. Environ. Pollut. J., 49: 37 – 51.

Jaradat Q.M and Mamoni K.A., 1999. Contamination of roadside Soil, Plants and Air With Heavy Metals in Jordan, A Comparative Study. Turk. J. Chem., 23:209 – 220.

Lagerwerff J.V. Specht A.W. 1970. Contamination of roadside soil and vegetation with Cadmium, Nickel, Lead and Zinc. Environ. Sci. Technol., 4:583 – 586.

Lindsay, W.L., Norvell, W.A., 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. Soil Sci. Soc. Am. J. 42, 421–428.

Mench, M.J., Didier, V.L., Loffler, M., Gomez, A., Masson, P., 1994. A mimicked in-situ remediation study of metalcontaminated soils with emphasis on cadmium and lead. J.Environ. Qual. 23, 58–63.

Morrison, R.D., 2000. Application of forensic techniques for age dating and source identification in environmental litigation. Environmental Forensics 1, 131-153.

Needleman, H., 2004. Lead poisoning. Annual Review of Medicine 55, 209-222.

Nriagu, J.O., 1993. Lead and Lead Poisoning in Antiquaity. John Wiley & Sons, New York.

Panichev, N.,Mandiwana, K. and Kataeva, M., 2005. Determination ofCr(VI) in plants by electrothermal atomic absorption spectrometry after leaching with sodium carbonate [J]. Spectrochimica Acta Part B 60(5): 699-703.

Qishlaqi, A., Moore, F., 2007. Statistical analysis of accumulation and source of heavy metals occurrence in agricultural soils of Khoshk River banks, Shiraz, Iran. American-Eurasian Journal of Agricultural and Environmental Science 2, 565-573.

ROPME; Manual of oceanographic observation and pollution analysis methods. ROPME, P. O. Box 26388,13124 Safat, Kwuait.; 1982.

Sahan, Y., B Basoglu, F., and Gucer, S., 2007. ICP-MS analysis of a series of metals (namely: Mg, Cr, Co, Ni, Cu, Zn, Sn, and Pb) in black and green olive sample from Bursa, Turkey [J]. Food Chemistry 105(1): 395-399.

Sandell, E.B. and H. Onishi, H., 1978. Photometric Determination of Traces of Metals: General Aspects. John Wiley & Sons, New York.

Shaw, M.J. and Haddad, P.R., 2004. The determination of trace metals pollutants in environmental matrices using ion chromatography [J]. Environment International 30(3): 403-431.

Turkmen, M. and Ciminli. 2007. Determination of metals in fish and mussel species by inductively coupled plasma-atomic emission spectrometry [J]. Food Chemistry 103(2):670-675.

WHO/FAO. 2007. Joint FAO/WHO Food Standard Programme Codex Alimentarius Commission 13th Session. Report of the Thirty Eight Session of the Codex Committee on Food Hygiene. Houston, USA, ALINORM 07/30/13.

Zeng, W. Chen, Y. and Cui, H., 2006. Single-column method of ion chromatography for the determination of common cations and transition metals[J]. J Chromatography A. 1118(1):68-72.

Zhang, C., Wu, L., Luo, Y., Zhang, H., Christie, P., 2008. Identifying sources of soil inorganic pollutants on a regional scale using a multivariate statistical approach: role of pollutant migration and soil physicochemical properties. Environmental Pollution 151, 470-476.